

The Johns Hopkins University

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DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS
UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

June 1921

JAN STEPHANUS VAN DER LINGEN



Baltimore, Md.
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THE FLUORESCENCE OF MERCURY VAPOR

By J. S. VAN DER LINGEN AND R. W. WOOD

ABSTRACT

The Fluorescent spectrum of mercury vapor cannot be excited in quiescent vapor, but only in vapor which is being distilled from the metal at a temperature of 150° or more. This proves that the active molecules are not neutral monatomic molecules but others present only during distillation, perhaps diatomic molecules. The spectrum consists of three lines— λ 2536, 2539, and 2346 Å—and four structureless bands with maxima at 2346, 2540, 3300, and 4850 Å. While the complete spectrum is excited by light from a zinc spark, single lines excite only part. The relation of the spectrum to the exciting light is of great interest. The broad bands with maxima at 3300 and 4850 may be excited, with varying relative intensity, by λ 1854-62, 2346, or 2536-40 Å; whereas the band λ 2346-2100 Å is excited only by λ 2000-2150 Å, the position of the maximum depending on the particular wave-length used. All the effective exciting lines lie, of course, in the absorption spectrum of mercury vapor.

The fluorescence of mercury vapor was first observed by Hartley while he was carrying out experiments on the absorption spectra of the elements and their compounds.¹

He found that the hot vapor, which was contained in an unexhausted quartz vessel, showed an absorption band which extended from 2526.8 Å to 2571.67 Å and that it fluoresced when it was excited by either a lead-cadmium or a tin-cadmium spark, the color of the fluorescent light being bluish green. He observed that the fluorescent light was most brilliant when the mercury was boiling briskly and that the fluorescence ceased when all the mercury had been converted into vapor above the boiling-point of the metal.

¹ *Proceedings of the Royal Society*, 76, 428, 1905.

From these observations he concluded, (a) that the phenomenon was not due to oxidation, because of the expulsion of the air during the brisk boiling of the metal, and (b) that there must be an upper and a lower limit of temperature between which fluorescence occurs.

Subsequently Professor R. W. Wood proved that mercury vapor *in vacuo*, at room temperature, shows two absorption lines, viz., 2536.7 Å and a fainter one at 2539.3 Å, and that these fuse together when the temperature is increased, while a band develops asymmetrically toward the red end of the spectrum, the head of the band remaining fixed at 2536.7 Å.¹ If air be introduced into the bulb, the head first grows symmetrically for about 8 angstrom units on either side of 2536 Å, and then extends toward the red end only. It was thus due to the presence of air that Hartley found the absorption band extending to 2526.8 Å. Wood also found that there are absorption lines at 2346.1, 2339, 2334.4, and 2331.2 Å and that these lines shaded off toward the violet end of the spectrum. If the density of the vapor be increased, these lines fuse together and form a band. The development of this band is difficult to trace because it is blotted out by the absorption band which heads from the absorption line 1849 Å to the visible spectrum. He found that the fluorescent spectrum of the vapor *in vacuo* is continuous and extends "roughly from the yellow down to wave-length 3000 with a very pronounced minimum at wave-length 3600," and that these bands show very little change, if any, when the vapor is excited by isolated lines of a spark spectrum. In addition to these fluorescent bands Wood found an emission line at 2536.7 Å, and a fainter companion line 2539.4 Å when the vapor is excited by an aluminum or cadmium spark, the emission being due to the last aluminum line and a group of cadmium lines which lie near the head of the 1849 absorption band. In the latter case, however, the emission line is much weaker than in the case of aluminum excitation. "This line appears strongest when the vapor density is such that the visible fluorescence does not quite appear. As the temperature is raised and the visible fluorescence grows stronger, the 2536 line fades away." Furthermore he showed that the fluores-

¹ *Philosophical Magazine* (6), 18, 240, 1909.

cence disappears when the vapor is superheated, and also when air is introduced into the bulb.

Immediately after the appearance of Wood's results Steubing published his observations on the fluorescence of mercury vapor, and he showed that not only is the mercury line 2536 Å emitted, but also the mercury line 2346 Å, when the vapor is excited by an aluminum spark. He also found a fluted band, which extends from this latter line to about 2100 Å. Furthermore he found that the ionization of the vapor was increased when it was excited by radiations lying within an absorption band of short wave-length. These results, he maintains, are in conformity with Stark's theory of absorption and fluorescence.¹

In 1914 Phillips² examined the resonance phenomenon of this vapor, which was discovered by Wood, i.e., the emission of 2536 Å when the vapor at room temperature is excited by 2536 Å of a water-cooled quartz-mercury arc. In order to determine the percentage of secondary resonance radiation, he allowed the vapor to distil past a horizontal slit and discovered that the vapor emitted 2536 Å as well as the fluorescent bands after it had passed out of the tract of the exciting light. He maintains that there are four fluorescent bands which from their position on his spectrum appear to be at the following positions approximately: (1) a diffused band at about 2700 Å; (2) heads on 3132 Å and ends at 3650 Å; (3) at 4360 Å; (4) a narrow band on the side of this region toward long wave-lengths. From what has been said it appears that mercury has absorption lines at 1849, 2346, and 2536 Å and three absorption bands: (1) heads from 1849 Å to the visible spectrum; (2) consists of the fused lines at 2346 Å which develop into a band; (3) extends asymmetrically from 2536 Å to the visible spectrum as the temperature is increased.

With regard to the work on the fluorescent bands and lines the results of the different observers do not agree.

OBJECT OF RESEARCH

The object of the following work was to find, as far as possible, the exact conditions under which mercury vapor fluoresces, and

¹ *Physikalische Zeitschrift*, 10, 787, 1909.

² *Proceedings of the Royal Society*, 89, 39, 1914.

also to determine the correlation between excitation in the various absorption bands and the emitted fluorescent lines and bands.

In the course of a somewhat extended study of the fluorescence of the vapor made by one of us, phenomena have from time to time been noticed which indicate that the fluorescence is not due to the monatomic mercury molecule. The evidence was thus summarized in a monograph on fluorescence not yet in print:

A thin-walled bulb, highly exhausted and containing a drop of mercury was heated in an Heraeus electric furnace and illuminated by an aluminum spark placed close to the bulb. The temperature of the furnace was determined by a nitrogen-filled mercury thermometer, placed close to the quartz bulb. With the temperature rising very gradually a very feeble fluorescence was observed at 150° C. while at 170° C. it was very bright. The density of the mercury vapor is increased less than twofold by this temperature increase, whereas the intensity of the fluorescence was certainly tenfold, if not more. On cooling the furnace, fluorescence disappeared entirely as soon as the temperature had fallen three or four degrees, though the density was much greater than that at which good fluorescence had been obtained with a rising temperature.

This makes it appear probable that something, diatomic molecules perhaps, commenced to come off the mercury at a temperature of 150°, the percentage of these fluorescing bodies increasing with rising temperature. As the temperature falls these bodies are no longer given off, and those already present disappear, probably by conversion into ordinary monatomic vapor.

The present investigation started out with a more careful study of this phenomenon. The experiment was repeated by using a similar quartz bulb which was placed over an asbestos chimney and gently heated by means of a Bunsen burner while a thermometer was placed over the bulb. On exciting the vapor by means of an aluminum spark placed near the bulb, it was found that the vapor exhibited faint fluorescence at 160° C., the intensity increasing rapidly with a rise of temperature.

On allowing it to cool, the fluorescence would cease at about 200°, and would only appear again on reheating up to 220° C. Very variable results were obtained by this method of heating, as was perhaps to be expected, but they verified completely the result of the earlier investigation, namely, that *the intensity of the fluorescence is a function of something other than the vapor-density.*

To secure a better control of temperature, an electric furnace was constructed of galvanized iron, lined with asbestos, the interior

being divided into two compartments by a vertical sheet of asbestos board. Two quartz bulbs joined by a short tube formed the mercury-vapor chamber, the tube passing through the asbestos partition. On either side of this partition an equal number of heating spirals were connected in series, and at the same time compensating spirals, having independent circuits, were fixed radially in each compartment. In this way the two connected bulbs could be kept at the same temperature, or a given difference of temperature between them could be established and held indefinitely. The exciting light entered the furnace as a parallel beam through a lateral hole, passing through the two bulbs and their connecting tube. In some cases the bulbs were illuminated one at a time by a beam entering the furnace at right angles to the axis of the bulb system. At constant temperature visible fluorescence could not be obtained; in other words, it was apparent that distillation must be going on in order to secure fluorescence. To settle this point definitely, the following very conclusive experiment was performed:

Two bulbs of very thin quartz, each about 1 cm in diameter, were joined by a short tube of quartz of about 1.5 mm bore. The two bulbs were mounted over a tall asbestos chimney, with a Bunsen burner at its base. The bulbs of two thermometers were placed immediately above the quartz bulbs. Operating under conditions avoiding air currents in the room, the two bulbs could be held at nearly the same temperature. One was always a little cooler than the other (about 5°) and in this one the liquid mercury of course collected.

When things had reached a steady state, say with one bulb at 200° and the other at 205° , both bulbs being illuminated by the light of an aluminum spark placed close to them, *no* fluorescence was observed. A blast of cold air, delivered through a small tube, was now directed against the hotter of the two bulbs, reducing its temperature enormously. The other bulb instantly flashed into a bright green fluorescence, which persisted until the last drop of mercury in it had disappeared, vanishing at the moment when distillation ceased.

The mercury was found now deposited as a dew on the cooled spot of the wall of the other bulb. The air current was now stopped and presently this bulb commenced to fluoresce as its temperature soon rose to its original value (205°) and the mercury began to distil back. No fluorescence was shown in either case in the bulb in which condensation was taking place. This was to be expected, as the pressure was lower in this part of the system.

However we interpret the results of this experiment, the fact is definitely established that only freshly formed mercury vapor is capable of exhibiting fluorescence.

This is not true of the resonance radiation described in previous papers by one of us, since mercury vapor in an exhausted tube at room temperature emits powerfully monochromatic light of wavelength $2536 \text{ \AA}$ when illuminated by light of this same frequency obtained from a water-cooled quartz-mercury arc. Now it is known from the previous investigation just alluded to that the same radiation is also emitted by comparatively dense mercury vapor (say 4 mm pressure) when it is illuminated by the spark lines in the region $1860\text{--}1870 \text{ \AA}$.

It seems therefore desirable to ascertain whether this emission depended also upon distillation. This radiation appears first at much lower vapor-densities than any at which visible fluorescence does, which suggests that it very probably results from the stimulation of monatomic mercury molecules, and does not depend upon the presence of diatomic molecules or other unique entities.

The presence of this radiation can of course be detected only by the quartz spectrograph. The double bulb just described was used as before, the spectrograph being directed at the hotter bulb (250°). An exposure of 2 minutes was given, the bulb being illuminated with the light of the aluminum spark. A faint trace only of the 2536 Hg line appeared on the plate: no visible fluorescence was observed. This experiment was now repeated, and after an exposure of 2 minutes had been given, the spectrograph was screened off and the mercury brought over into the hotter bulb by an air blast. On removing the blast, the mercury commenced to distil back, and visible fluorescence occurred. Exposures were now made on the same plate of 2, 4, 6, and 8 seconds' duration.

On developing the plate it was found that the exposure of 2 seconds with the vapor distilling recorded the 2536 line with the same density as the 2 minutes' exposure of the stagnant vapor. This indicates that the 2536 emission line, excited by the short-wave-length spark lines, results in all probability from the stimulation of the entities which give rise to the visible fluorescence, but that a few of them are present even in the stagnant vapor, distillation increasing their number about sixty fold.

We will now consider the relation which exists between the wave-length of the exciting light, and the distribution of intensity among the various fluorescent bands and lines.

The absorption of mercury vapor is rather complex, and as one or two points in regard to it were still somewhat obscure, the investigation commenced with a study of this phenomenon. Combining previous work with our supplementary observations we arrive at the conclusion that the absorption spectrum is as represented in Figure 1*a*, viz.:

1. A strong absorption line at 2536 Å, and a weaker one at 2539 Å.

2. Four lines at 2346, 2339, 2334, 2331 Å which fuse together with rise of temperature, forming a band which gradually pushes toward the side of short wave-lengths with increasing vapor-density.

3. There is in addition a strong absorption line at 1849 Å corresponding to the powerful emission line at the same point.

4. Two strong and very asymmetrical absorption bands, one with its head in close proximity to the 2539 line and the other with its head near 1849 Å. These bands creep out gradually, with increasing vapor-density toward the region of longer wave-lengths.

The complete fluorescence spectrum, which, for reasons which will be explained presently, is given by excitation with the zinc spark, is shown diagrammatically in Figure 1*b*.

It consists of: (1) a symmetrical structureless band, extending from the red down to wave-length 3700, with its maximum at 4850 Å; (2) a similar broad band with a maximum at 3300 Å, the two fusing together with long exposure; (3) an asymmetrical faint band coinciding with the absorption band just above 2539; and (4) a somewhat asymmetrical band extending from 2349 to 2100 Å.

There are in addition the lines 2536 Å and 2539 Å, which, however, are not very strongly developed with the zinc spark.

It is of the utmost importance to find out how the absorption bands and lines are related to the fluorescent emissions.

For the examination of this point it is necessary to excite the vapor with monochromatic radiation or groups of such radiations lying in different regions of the absorption bands.

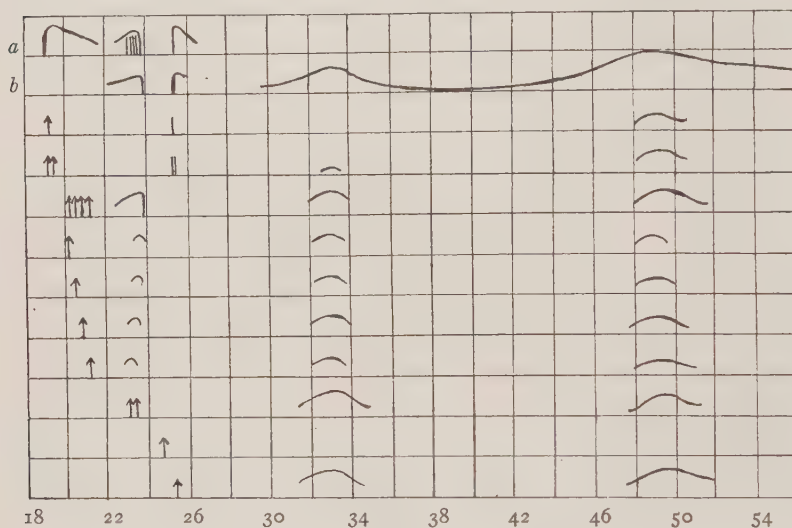


FIG. 1

a, absorption spectrum

b, fluorescent spectrum due to excitation by zinc spark

↑, exciting lines

|, emission lines

Two methods have been employed for the isolation of such radiations, viz., prismatic decomposition of the light of the spark by means of two large quartz lenses with a quartz prism, and the method of focal isolation employed by Rubens and Wood for the isolation of very long heat waves.

In the former case two quartz lenses of 8 cm aperture and 50 cm focus were used in conjunction with two Cornu prisms, mounted on top of one another. In this case the bulb was placed immediately behind a tin screen, perforated with a slit and coated with

Willemite, on which the spark lines were focused. This screen rested on the funnel beneath which the Bunsen burner was placed, and the bulb was placed immediately behind the slit. By moving the quartz lens any desired spectrum line could be passed through the slit to the bulb.

In the second case the central portions of each lens were screened off by means of a black paper disk. The axes of the lenses and the spark were placed in line with a small, circular hole in a metal screen, coated with Willemite, behind which the bulb was placed. The desired groups of rays were then focused so as to pass through this hole on to the bulb. The object of the disk was of course to cut out the central beam of light.

This second method gives greater intensity of illumination, as the absorption of the prism is avoided, the full aperture of the lenses is utilized, and the greater transparency of the thin edges of the lenses for the very short wave-lengths comes into play. It suffers from the disadvantage that only a rather wide group of radiations can be isolated. Focal isolation with mercury fluorescence clearly shows the presence of the group of weak zinc lines between 1900 Å and 1860 Å. These lines are absorbed by the monochromator to such an extent that they have no effect on either the Willemite screen or the mercury vapor. To avoid the possible absorption of the fluorescent light by the vapor, the quartz spectrograph was directed toward the face of the bulb where the light entered in such a direction that little of the exciting light was reflected into the spectroscope. This condition was obtained by reducing the diaphragm of the spectroscope and observing the bulb through the instrument (eye placed at the focus) and arranging matters in such a way that none of the spark images seen reflected from the bulb walls fell within the aperture of the diaphragm.

EXCITATION IN THE 1849 ABSORPTION BAND

This absorption band begins at wave-length 1849 Å and extends toward the visible spectrum with increase of vapor-density, reaching 2200 Å at about 280° C., with a column of vapor 10 cm in length.

On separating the aluminum lines by means of the monochromator and allowing Al 1854 to excite the vapor, it was found that visible fluorescence first appeared at 210° C. and that the slightest increase in the temperature caused the fluorescent beam to recede to the face of the bulb.

On photographing the emission spectrum it was found that the excitation caused the emission of the 2536 line, and the continuous band in the green-violet (maximum at 4850). On increasing the density and photographing the emission spectrum again, it was found that the 2536 line was weaker, the green-violet band was more intense, and the ultra-violet band (maximum intensity at 3300 Å) now appeared and grew stronger as 2536 Å decreased in intensity. No trace of the 2539 line appeared, though this may have been due to insufficient exposure.

From this it appears that excitation at low vapor-density, with radiation at the head of the extreme ultra-violet band, causes a concentration of the emitted energy in the green-violet band; at higher vapor-density, however, the ultra-violet band appears and the 2536 line fades away. The same thing was observed if the excitation was caused by the Al lines in the region 1854–1862, though in this case there was a trace of the ultra-violet band, even at the low density, while at the higher density it was nearly as strong as the green-violet band. The development of the ultra-violet band is thus seen to be favored by excitation in a region a little removed from the head of the band.

It must be understood, however, that the wide ultra-violet absorption band may be a complex of several bands, each one associated with an emission band. If this were the case, we should then have the green-violet band associated with the component of the ultra-violet absorption band which falls just above the 1849 line, the ultra-violet emission band with a component of the absorption of somewhat longer wave-length, and if there were a third component of still longer wave-length, and we excited in this region, we should expect a third fluorescent band still farther down in the spectrum.

This is, in fact, the case, because on excitation by the group of *in*zc lines in the region 2000–2150 Å we find a new fluorescent band,

not previously described, in the region 2349 to 2100. This band occupies approximately the position of Steubing's fluted band, of which we have never been able to find any trace. In addition, we find a trace of 2536 Å and 2539 Å and a faint band with its head at 2539 Å which corresponds to the absorption band shown in Figure 1a.

The newly discovered fluorescent band at 2346 Å behaves in a manner quite different from that of the bands in the green-violet and upper ultra-violet.

This band is excited in its entirety by the group of four zinc lines 2024, 2061, 2909, and 2138 Å. If these are separated by the monochromator and the excitation is produced by each in turn, it is found that the region of maximum intensity in the new ultra-violet band moves to the violet end of the spectrum as the exciting line moves toward the visible end of the spectrum, i.e., excitation by the zinc line of shortest wave-length gives us only the portion of the emission band of longer wave-lengths, while excitation by the zinc line of longest wave-length gives only the short-wave-length portion of the band. Expressing this in other words, when we excite by the zinc lines in succession (increasing wave-length), the emission band moves down toward the excited region. If now we move the exciting wave-length still farther up the spectrum, utilizing a group of cobalt lines in the region of the group of absorption lines at 2346 Å, we obtain the green-violet band and the next ultra-violet band (3300) of uniform intensity. The same is true if we excite with the monochromatic radiation of the 2536 Hg line obtained from the water-cooled mercury arc.

There is left now only the absorption band just above 2539 Å. If we form an image of the two strong zinc lines (one of which lies to the right and the other to the left of the 2536 Hg line) on the surface of the quartz bulb, we find on heating the bulb that the zinc line of longer wave-length causes fluorescence. This line falls within the absorption band above referred to. The spectroscope shows that in this case we have also the green-violet and ultra-violet bands of uniform intensity.

On exciting the vapor by all the aluminum lines lying below 2360 a faint line appeared at 2346 Å when the vapor was distilling

slowly. On increasing the vapor-density this line increases in intensity, but is soon blotted out by the extreme ultra-violet band which increases relatively faster in intensity than the line. In addition to the emission of 2346 Å, first observed by Steubing, and the band in this region, 2536 Å, 2539 Å and the green-violet and ultra-violet bands are emitted.

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VITA

Jan Stephanus van der Lingen, third son of Godlieb Wilhelm Brückner and Susanna Sophia (Moll) van der Lingen, was born at Kroonstad O.F.S., South Africa, on December 12, 1887. He received his early education in the local public school until the time of the British occupation of Kroonstad during the Anglo-Boer War, when he together with his parents, were deported to East London. On his return after the cessation of hostilities, he rejoined the school for some time and then apprenticed himself to Jacobson Brothers, electrical engineers and soon became the foreman electrician of the firm. In 1907 he re-entered school and graduated from high school at the end of the year. In 1908 he joined the Victoria College, Stellenbosch, and for the four years following studied experimental physics, applied mathematics, mathematics, chemistry, classics, and modern languages, obtaining the Honor Certificates of this institution for B.A. Honors physics 1910 and B.A. Honors applied mathematics in 1911, when the degree of Bachelor of Arts with Honors was conferred upon him by the University of the Cape of Good Hope.

Pending his departure for Europe as government scholar he acted as *locum tenens* in the following positions: vice-principal and science master at the Boys' High School, Cradock, Cape Colony; science and mathematics master at the public school, Kroonstad, O.F.S.; lecturer in applied mathematics, South African College, Cape Town.

In 1913 he studied in the Polytechnikum Zurich, Switzerland, under Professors Moos (engineering), Einstein (physics), Bauer (physical chemistry), and in the Zurich University under v. Laue (physics), Greinacher (physics), and Priv. doz. Ratnowski (physics), Wolfer (astronomy), Zermelo and Bernays (mathematics).

His researches during this period (1913-14) were published in the *Physikalische Zeitschrift*; *Die Naturwissenschaften* and *Verhandlungen der Deutschen Physikalischen Gesellschaft*.

In 1913 he obtained the Duke of Cornwall and York prize for his thesis on *The Space Trellis of Liquid Crystals* (Adjudicator Bragg) and became a member of the Royal Society of South Africa and Mitgleid der Deutschen Physikalischen Gesellschaft. In June, 1914, he was invalided home owing to Röntgen dermatitis. In September, 1914, he was reappointed lecturer in applied mathematics at the South African

College, Cape Town, and in 1920 was promoted to Senior Lecturer, University of Cape Town (formerly S. A. College). During these years his researches were published in the *Transactions of the Royal Society of S.A.* and the *S.A. Journal of Science*.

From 1914-19 he was a member of the Research Grant Board of the Royal Society of S.A.

He is a member of the following societies: Franklin Institute, Pennsylvania, U.S.A.; Royal Society, South Africa; Deutsche Physikalische Gesellschaft; Schweizerische Natforschende Gesellschaft; Fellow, Physical Society of London; Röntgen Society, London; Scientific and Engineering Society (Univ. Cape Town) (President, 1917-20); Afrikaanse Wetenskaplike Vereniging (President, 1918-20).

In 1919 he was elected Government Research Scholar. In 1920 he was elected James Buchanan Johnston Scholar at the Johns Hopkins University, Baltimore, Maryland, U.S.A., where he studied under Professors Ames, Wood, and Pfund (physics); Professor Reid (geophysics); Professor Murnaghan (applied mathematics).

